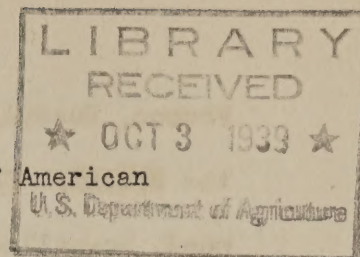# Composition of the Non-Pinene Portion of American Gum Turpentine.

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ment of Agriculture.

Turpentine has for years been almost inseparably associated
with paint. Even though today, when paint manufacturers also are
using other solvents and thinners, the greatest industrial outlet
for turpentine is still the paint and varnish industry. In con-
nection with its use in paint, comparatively little thought is
given to its composition and to the unique chemical and physical
properties of its major constituents, the pinenes, or to the
less volatile minor constituents which are known to exert con-
siderable influence in the behavior and reactions of the pinenes
themselves.10/ Turpentine is in reality a mixture of highly reac-
tive chemicals belonging almost entirely to the terpene group.
Its potentialities as raw material for the isolation of organic
chemicals, for the preparation of diverse derivatives, for the
synthesis of chemicals which may find application as plastics,
as synthetic resins, as perfumes, and as medicinals, is only now
being appreciated.

Commercial turpentine may be roughly divided into two gen-
eral types, that produced from gum and that derived from wood.
The gum spirits type is distilled from the oleoresin of the liv-
ing tree, and in this country is obtained principally from the
two species, P. Palustris and P. Caribbaea (longleaf and slash
pine, respectively). A substantial part of the world's gum spir-
its of turpentine is obtained from other species of pines in

France, Russia, Greece, Spain, Portugal, and, to some extent in the Orient. Turpentines of the second type are produced from wood, so-called "steam distilled wood turpentine" being the most important representative. Both it and destructively distilled wood turpentine are derived from old pine stumps and lightwood. The pulping of pine wood by the sulfate process also yields turpentine as a by-product. The composition and properties of the wood turpentine vary with the different producers and degree of refinement. In contrast with the turpentines of the second type, production of which is mainly in the hands of well-organized and modern chemical industries, the gum spirits type is produced almost entirely in a more or less primitive way. The farmer-producer, with his individual still, is his own producer of turpentine and rosin. There are some 1,200 stills distributed in the pine belt. There is, consequently, a sharp difference in the picture presented by the gum industry, which is turning out turpentine as such, and the more recently developed wood turpentine industry, which now offers a host of chemical products and is constantly increasing and diversifying these products. This does not mean, however, that gum turpentine is not used as a raw material in a few synthetic chemical industries, such as manufacture of synthetic camphor, and to a very limited extent (abroad), manufacture of terpineol and terpin-hydrate. In the synthetic field, however, it is used only in a very restricted way, and as a competitive raw material with other turpentines.

As a prerequisite for the production and commercial exploitation of its various chemical products, the wood turpentine industry has found it necessary to make an intensive study of the composition

of its raw materials. To this day it is characterized by continuous activity in the isolation of constituents and preparation of derivatives. A great deal of fundamental information on this type of turpentine has thus become available. Contrast this with the gum industry. Although it still constitutes the major supply of turpentine, little fundamental study -- and most of this comparatively recent -- has been given gum spirits of turpentine. In fact, until a few years ago, beyond the work of Darmois, [4] Dupont and Barraud, [7] and Palkin, [9] comparatively little was known regarding the composition of even the major terpene constituents, α- and β-pinene. These two are now known to represent about 95 per cent of the fresh gum spirits. Information on the remaining 5 per cent is exceedingly meagre, despite the fact that it has long been known that this portion exercises an influence, disproportionate to its percentage content, in the yield of synthetic camphor, and despite the fact that the characteristic pleasant aroma of fresh gum spirits was highly indicative of promising constituents in this turpentine.

In a publication a few years ago, [9] composition of the major part of American gum spirits was reported. In a later publication [13] a detailed study of the composition of commercial steam distilled wood turpentine was reported, and gross differences in the composition of the two kinds of turpentine were pointed out. This comparative study, however, was handicapped by the absence of information on the nature and constituents of the non-pinene portion of gum spirits. The work reported in the present paper is an attempt to fill in this much needed information on the minor constituents of gum spirits comprising both low-boiling and high-boiling constituents, generally referred to as the "forerun" and "tailings," respectively. The low-boiling part, or "forerun," although con-

stituting but an insignificant proportion together with the "tail-ings," may exercise an important contributory influence on the keeping qualities of turpentine.

Dupont[4] has examined French turpentine, which resembles American gum spirits of turpentine, and detected dipentene, sobrerol, possibly pinol, a sesquiterpene hydrocarbon distilling around 220°C/10 mm, traces of alcohols, and traces of aldehydes or ketones.

While our own investigation was in progress Hasselstrom and Hampton reported in a recent communication[8] finding methyl chavicol in gum spirits tailings. The presence of methyl chavicol was also known to us. The occurence of methyl ethers was mentioned in our preliminary report on the subject.[16]

The composition of the tailings, exclusive of non-volatile matter such as rosin carried over by entrainment, is roughly as follows:-

(a) About 1/5 consists of hydroxy compounds (alcohols and phenols). A detailed study of the composition of this portion is not being reported at this time.

(b) About 2/5 consists of monocyclic hydrocarbons, dipentene, terpinolene, and possibly p-menthene and limonene. The saturated hydrocarbon p-menthane could not be detected.

(c) About 2/5 consists of other non-hydroxy compounds which distill above 85°C/10 mm, and do not react with alkyl borates. A considerable proportion of this is methyl chavicol, the lower boiling isomer of anethol. Methoxyl determinations of higher boiling fractions also indicate other methyl ethers or esters. Bornyl acetate has been separated and identified. The examination of the material boiling above 100°C/10 mm has not been completed.

Experimental

<u>Distillation Procedure and Equipment.</u> The fractionations were carried out in distillation assemblies at suitable pressures maintained constant by a sensitive pressure control mechanism.[11] Operation at accurately reproduced and controlled pressures[2] rendered changes in distillation temperatures of less than 0.1°C significant, thus permitting a more intelligent "cutting" of the distillate into appropriate fractions. Temperature changes were read by means of a multiple thermocouple connected through cold junctions to each other and to a potentiometer. Temperature served as a guide in the properly timed introduction of individual fractions into the still pot for systematic refractionation.

The major portions of the fractionations were carried out in gauze plate columns, the one shown in Figure I being a typical assembly. The columns were surrounded with hot air jackets similar to the one described by Bruun.[1] In the latter part of the distillation work, particularly in the fractionation of high-boiling liquids at low pressures, use was made of a wound glass fiber anti-bumping and boiling promoting device.[12] Some of the final refractionations of the forerun were carried out in a semi-micro packed column.[13]

The initial fractionations were run in batches. As the elimination of the pinenes progressed, it was possible to combine concentrates of the minor constituents. These composites were then systematically refractionated.

"Heads," or Forerun. The turpentine used for this part of the investigation represented the first 10 per cent of the steam distillate of a commercial charge of longleaf pine oleoresin (P. Palustris). Dissolved water was removed as ice by chilling to -20°C. The turpentine thus dehydrated had the following properties; Sp. gr. $\frac{15.5}{15.5}$, .8663; n_D^{20}, 1.4698; a_D^{20}, +16.8; Engler distillation, initial 153°C, 98 per cent distilled below 165°C.

The turpentine was then subjected to systematic fractional distillation under reduced pressure. The more highly volatile material which passed the water condenser was collected in a dry ice trap. Only compartment "a" of the dry ice trap of Figure 1 was packed with dry ice. The "heads" from 31 kilograms of turpentine were thus concentrated into three fractions. These concentrates, still containing large proportions of a-pinene, had the following properties:

Table I.

Fraction	Wt. (Gms.)	Boiling Range °C.	Optical Rotation [1] a_D^{20}
1	19	53-70 (51 mm)	+15.5
2	78	62-63.5 (34 mm)	+27.5
3	76	63 5-63.7 (34 mm)	+29.5

[1] The pure a-pinene was found to have a rotation of +31.0°.
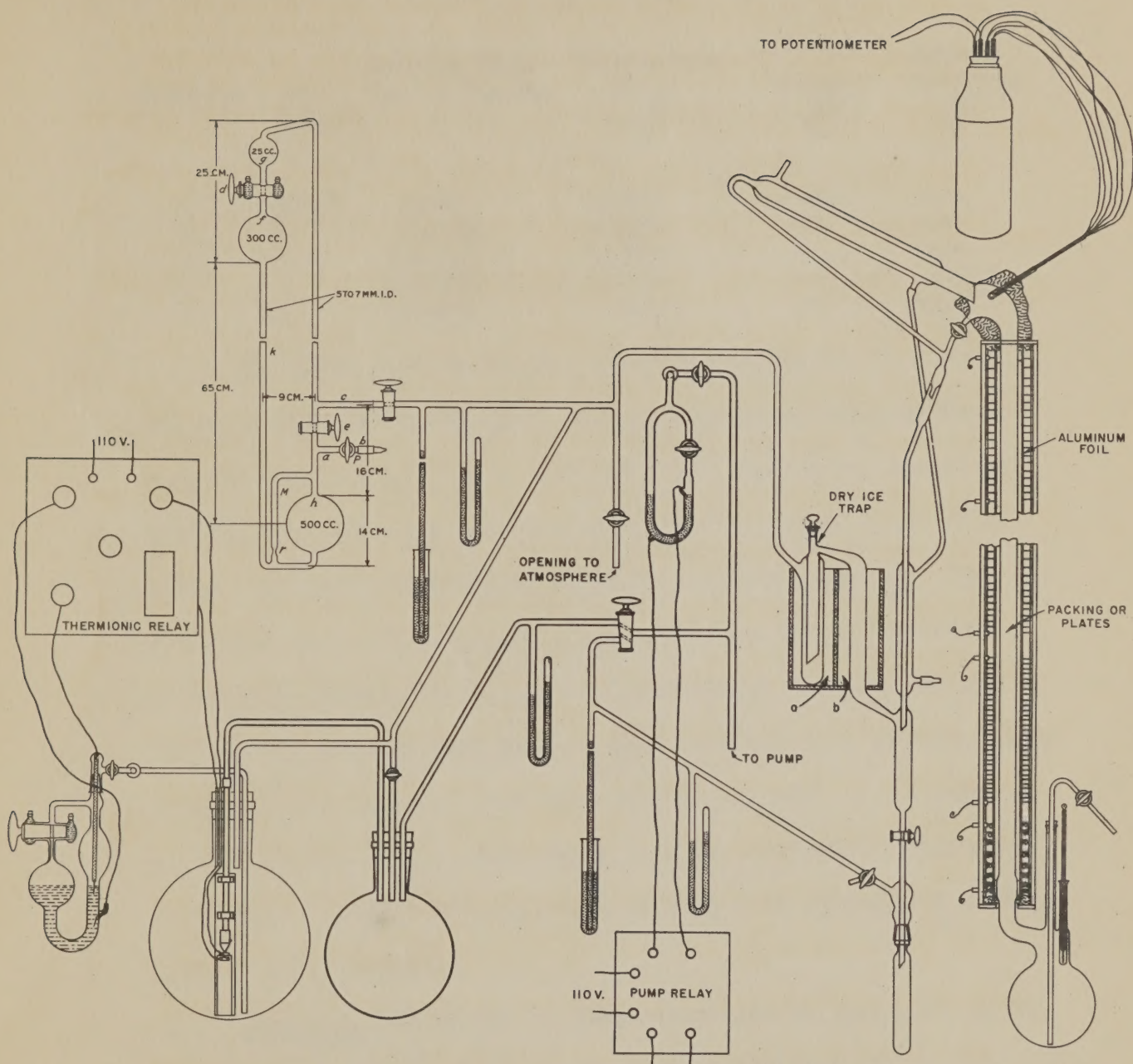
Figure 1.   Fractionating Assembly.

Figure 1. Machining Assembly.

After four systematic refractionations, a new series of
fractions was obtained, of which the following are the five top
fractions:

Table II.

Fraction	Wt. (Gms.)	Boiling Range °C. at 760 mm	Refractive Index n_D^{22}	Density d_4^{20}	Optical Rotation α_D^{20}
1	3-1/2	56-63	1.3776	0.800	---
2	4	63-102	1.4105	---	---
3	4	102-120	1.4400	---	---
4	4	120-145	1.4485	---	---
5	12	145-156	1.4630	---	+24.6°

The first four fractions, totaling only 15 cc, represent
the major part of the "heads," or portion boiling below α-pinene.
Each fraction boiled over a wide range of temperature, indicating
that no pure compounds have been separated in any of these frac-
tions. The fifth fraction is about 80 per cent α-pinene. The
results of this distillation indicate that the total "forerun"
or material boiling below α-pinene constitutes at most, .07 per
cent of the original turpentine. This is taken as a maximum, since
the sample was obtained from the first 10 per cent of a charge,
and was somewhat richer in forerun than the commercial turpentine
as a whole. Further investigation of this part is awaiting collec-
tion of larger samples.

Tailings. The sample of turpentine used in this part of the
investigation was a portion of the last 10 per cent (2) of turpentine
distilled from a commercial distillation of longleaf oleoresin
(P. Palustris)

10/

(2) This portion was collected because it has been found that the
last 15 per cent of spirits contains a higher proportion of
β-pinene and tailings than does commercial gum spirits. The
Darmois 9/ method of calculation indicated that this sample
contained about 45 per cent α-pinene, about 47 per cent
β-pinene, and 7.7 per cent tailings.

The turpentine had the following constants:-

Sp. gr. $\frac{15.5}{15.5}$, .8747; n_D^{20}, 1.4739; α_D^{20}, +3.9; Engler distillation, 89 per cent distilled below 170°C.

In order to remove rosin carried over by entrainment during the commercial distillation, the turpentine was redistilled with steam. The residue was then subjected to vacuum distillation, and the portion which did not distill below 100°C. at 1 mm was considered "non-volatile." Examination of this non-volatile residue, amounting to 0.4 per cent of the original turpentine, showed it to be principally resin acids.

Twenty-six kilograms of this redistilled turpentine was subjected to repeated fractional distillation in order to eliminate the pinenes (3) and to effect a concentration of the tailings. After several refractionations, a series of 50 fractions, boiling above β-pinene and totaling 2 kilograms, was obtained, and these are listed in Table III. The physical properties of these fractions are shown graphically in Figure 2. A number of compounds were obtained in high concentrations in various fractions, as indicated in Table III, and evidenced by breaks in the curves in which the progressive change in properties were plotted in terms of per cent distilled.

Progress in the separation of the hydrocarbons from the alcohols and methyl ethers also was followed by the determination of hydroxyl by the Zerevitinoff[14,17] method, and of methoxyl by the Viebock and Schwappach method as modified by Clark[3].

(3) A previous investigation[9] has shown that, except for the small amount of forerun, the fractions distilling below the tailings contain only α-pinene and β-pinene.

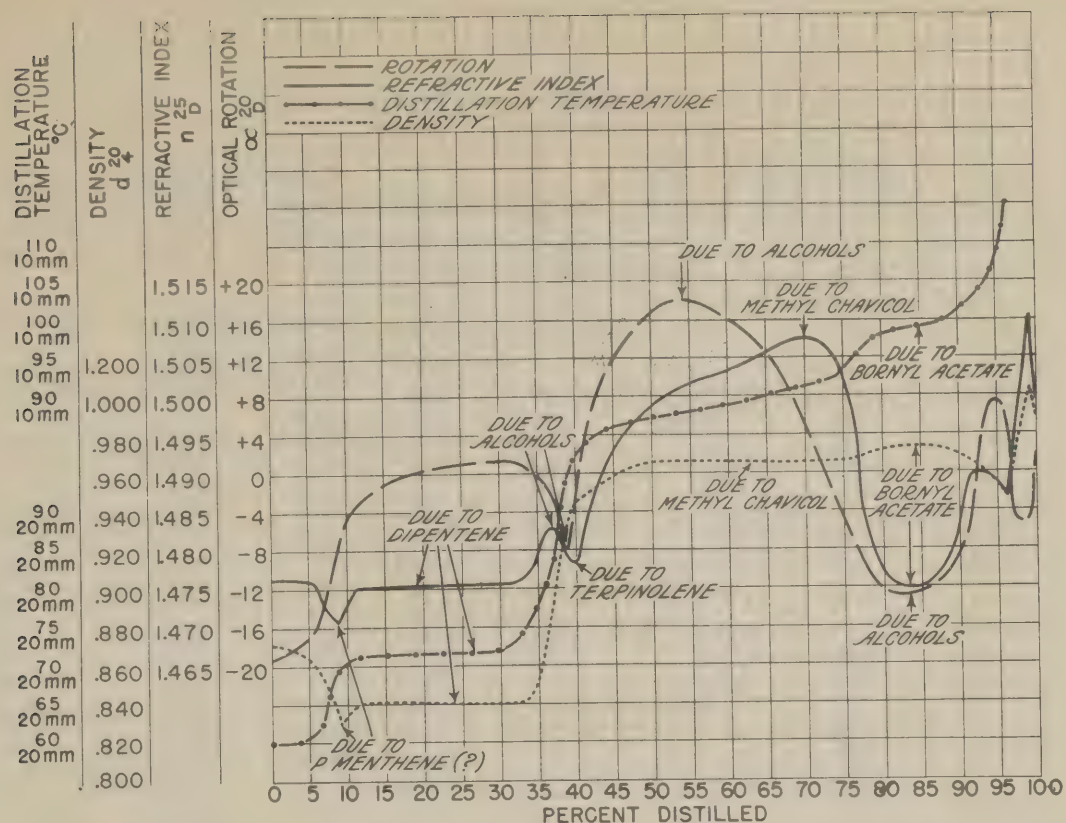**Figure 2.** Properties with Respect to Percent by Weight of Fractions of Tailings (Table III).
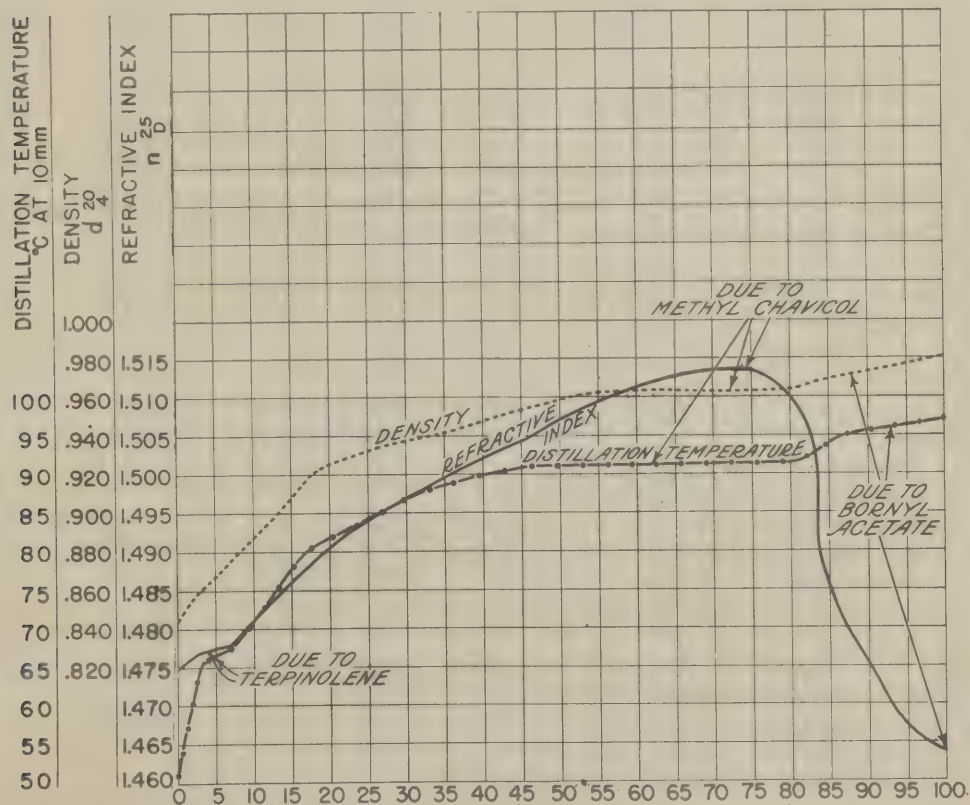

Figure 3. Properties with Respect to Percent by Weight of Fractions of Alcohol-Freed Tailings Distilling between 65 - 100° C/10 mm. (Table V)

TABLE III.

Physical and Chemical Properties of Tailings Fractions

Fraction No.	Distillation Temperature °C/20 mm	Refractive Index n_D^{25}	Optical Rotation α_D^{20}	Density d_4^{20}	Hydroxyl % [a]	Methoxyl % [b]	Ratio each fraction to Total Tailings %	Sum of Fractions %	Ratio each Fraction to Turpentine %
1	59.7-60.0	----	-18.2	----	----	----	3.6	3.6	0.28
2	60.0-61.0	1.4760	-16.20	.8613	----	----	2.1	5.7	0.16
3	61.0-64.0	1.4743	-13.12	.8480	----	----	1.6	7.3	0.12
4	64.0-69.0	1.4732	- 8.20	.8283	----	----	1.6	8.9	0.12
5	69.0-70.5	1.4743	- 5.41	.8352	----	----	1.0	9.9	0.08
6	70.5-71.0	1.4751	- 3.18	.8398	----	----	1.4	11.3	0.11
7	71.0-71.3	1.4753	- 1.60	.8405	----	----	1.7	13.0	0.13
8	71.3-71.5	1.4752	- 1.05	.8413	----	----	2.0	15.0	0.15
9	71.5-71.7	1.4754	- 0.30	.8413	----	----	1.8	16.8	0.14
10	71.7-71.7+	1.4759	+ 1.15	.8412	0.05	0.2	11.1	27.9	0.85
11	71.7+-72.0	1.4756	+ 1.51	.8411	----	----	1.5	29.4	0.12
12	72.0-73.0	1.4756	+ 1.52	.8408	----	----	2.4	31.8	0.18
13	73.0-76.0	1.4771	+ 0.51	.8421	0.2	----	1.8	33.6	0.14
14	76.0-85.0	1.4829	- 2.80	.8813	1.4	0.2	3.5	37.1	0.27
15	85.0-93.0	1.4791	- 7.98	.9313	2.6	----	1.4	38.5	0.11
16	93.0-97.0	1.4784	- 4.82	.9444	----	----	1.3	39.8	0.10
17	97.0-98.6	1.4834	+ 2.80	.9484	6.0	2.8	1.3	41.1	0.10
18	98.6-99.7	1.4881	+ 7.00	.9525	----	----	1.3	42.4	0.10
19	99.7-100.6	1.4909	+ 9.90	.9557	----	----	1.4	43.8	0.11
20	100.6-101.1	1.4939	+12.05	.9616	6.2	4.3	1.4	45.2	0.11
21	101.1-101.3	1.4953	+13.81	.9622	----	----	1.4	46.6	0.11
22	101.3-101.6	1.4969	+15.40	.9636	----	----	1.4	48.0	0.11
23	101.6-102.0	1.4981	+16.38	.9652	5.6	7.0	1.4	49.4	0.11
24	102.0-102.2	1.4993	+17.18	.9655	----	7.4	1.2	50.6	0.09
25	102.2-102.4	1.5004	+17.80	.9662	----	7.9	1.4	52.0	0.11
26	102.4-102.6	1.5013	+18.07	.9667	5.5	8.5	1.4	53.4	0.11
27	102.6-103.3	1.5025	+16.20	.9648	----	9.8	5.0	58.4	0.38
	°C/10 mm								
28	89.0-89.5	1.5036	+15.59	.9650	----	10.6	3.0	61.4	0.23
29	89.5-90.0	1.5051	+13.07	.9649	3.7	11.8	3.0	64.4	0.23
30	90.0-90.5	1.5059	+10.80	.9646	----	12.3	2.4	66.8	0.18
31	90.5-91.0	1.5076	+ 5.30	.9644	2.8	13.4	2.6	69.4	0.20
32	91.0-91.5	1.5071	+ 2.85	.9647	2.8	11.2	1.4	70.8	0.11
33	91.5-92.0	1.5068	- 0.43	.9647	----	10.7	1.9	72.7	0.15
34	92.0-92.5	1.5031	- 3.86	.9652	----	----	1.8	74.5	0.14
35	92.5-95.0	1.4941	- 6.95	.9657	----	----	2.0	76.5	0.15
36	95.0-97.0	1.4825	-10.28	.9691	3.6	3.5	1.7	78.2	0.13
37	97.0-98.0	1.4764	-12.50	.9705	----	----	2.0	80.2	0.15
38	98.0-98.4	1.4753	-12.90	.9715	4.8	----	1.6	81.8	0.12
39	98.4-98.7	1.4751	-12.70	.9725	4.6	0.4	1.6	83.4	0.12
40	98.7-99.0	1.4751	-12.35	.9718	----	----	2.2	85.6	0.17
41	99.0-99.5	1.4775	-11.53	.9713	5.3	----	1.6	87.2	0.12
42	(at 10 mm (99.5-100.0	1.4793	-11.00	.9708	----	----	1.3	88.5	0.10
43	(at 5 mm (87-91	1.4821	- 8.73	.9682	----	----	1.2	89.7	0.09
44[c]	----	1.4900	- 1.00	.9670	8.1	0.5	2.0	91.7	0.15
45	(at 10 mm (103-104.2	1.4887	+ 0.82	.9609	7.2	0.3	1.5	93.2	0.12
46	(at 10 mm (104.2-106.5	1.4891	+ 7.40	.9534	7.5	0.3	1.4	94.6	0.11
47	(at 5 mm (94-101	1.4871	+ 4.10	.9472	6.8	1.3	1.5	96.1	0.12
48	(at 5 mm (101-107	1.4943	- 5.45	.9682	5.7	7.6	1.1	97.2	0.08
49	(107 at 5 mm to (103 at 3 mm	1.5105	- 5.51	1.004	3.1	20.5	1.7	98.9	0.13
50 (Residue)	----	1.4965	+ 1.88	.9879	6.2	1.9	1.1	100.0	0.08
							100.0		7.68

[a] Theoretical hydroxyl equivalent of $C_{10}H_{17}OH$ equals 11.03%.

[b] Theoretical methoxyl equivalent of $C_9H_9OCH_3$ equals 20.95%.

[c] Fractions 45-50 were not included in the final refractionation because of their high boiling points. Fraction 44 is the residue from the final refractionation of the tailings.

Interpretation of plotted data shown in Figure 2. Breaks in
both the density and the refractive index curves between 5 per cent
and 10 per cent points indicated that there had been a concentra-
tion of some compound, the properties of which pointed to the
saturated cyclic hydrocarbon, p-menthane, a compound previously
identified in steam distilled wood turpentine. Because of the
small quantity available and the presence of substantial propor-
tions of β-pinene, it was not possible to obtain this compound pure
by further fractionation. However, a portion of fraction 4, Table III,
was found to dissolve completely in mild fuming sulfuric acid, in-
dicating the absence of stable saturated hydrocarbon. The most
probable unsaturated compound appears to be p-menthene. An attempt
was made to prepare a nitrosyl chloride, but none could be isolated,
probably due to the admixture of both β-pinene and dipentene.

Dipentene. Flat portions on all the curves between 10 per
cent and 35 per cent points in the distillation are due to the
separation of dipentene. The slight slope of the rotation graph
can probably be attributed to the presence of a small amount of
active limonene. The dipentene was identified as the tetrabromide.

A maximum appears on the refractive index and a minimum on
the optical rotation curve in the region of the 37 per cent point.
Hydroxyl determinations indicate that the fractions in this region
contain approximately 20 per cent terpene alcohols (See Table III).
These changes may be due to the appearance of the terpene alcohol.

The minimum in the refractive index curve at the 40 per cent
point and the flattening of the density curve near this point are
due to terpinolene, which was identified as described later.

About 35 per cent of the tailings was found to be a mixture of methyl chavicol and terpene alcohols distilling over a 10°C range. While the density curve in this region (42-77 per cent points) is nearly flat, and would appear to indicate a pure compound, this, however, is only apparent, due to the fact that methyl chavicol and the terpene alcohols have approximately the same densities. The refractive index curve has a maximum at 70 per cent point and methoxyl determinations (See Table III) show that methyl chavicol reaches a maximum of 64 per cent at this point. The rotation curve has a maximum at 54 per cent point. This is in agreement with hydroxyl determinations which show that the amount of terpene alcohol reaches a maximum of about 50 per cent at this point, the maximum in the rotation curve at this point presumably being due to concentration of alcohols.

The distillation curve flattens out between 80 per cent and 87 percent points, the density curve has a maximum, and the refractive index has a minimum. These effects are due to the concentration of inactive bornyl acetate (4), the identification of which will be described later.

Hydroxyl determination (Table III) shows that the quantity of terpene alcohol passes through a minimum at the 72 per cent point, the point at which the rotation curve crosses the zero rotation line. After reaching a minimum the quantity of terpene alcohols again increases as the negative rotation increases.

(4) Greek turpentine 5/ contains about 1 per cent inactive bornyl acetate.

The per cent hydroxyl continues to increase, while the rotation curve passes through a minimum and reaches a maximum at the 95 per cent point. Near this point, the rotation curve has a maximum and the refractive index and density curves have a minimum.

The refractive index and density curves have a maximum near 99 per cent point and the rotation curve has a minimum. The per cent methoxyl reaches a maximum at this point also. These effects are without doubt due to another methyl ether of some type. The minimum in the rotation curve may be due to a change from one alcohol to another. The percentage of hydroxyl passes through a minimum at this point.

All the higher boiling fractions were tested for phenols with diazo-p-nitrobenzene.[13/] Fractions 46 to 50, inclusive, Table III, gave positive tests, indicating that at least part of the hydroxy compounds in these fractions was phenolic.

<u>Chemical Separation of the Alcohols and a Study of the Non-Alcohol Portion Distilling below 100°C at 10 mm.</u> Since hydroxyl determinations showed that the first 34 per cent of the tailings contained very little terpene alcohol, the chemical separation of the alcohols was confined to the portion between 34 per cent and 89 per cent points. The thirty fractions involved were recombined into five portions, and each portion was treated with butyl borate for the separation of alcohols.

After determining active hydrogen by the Zerevitinoff method, 1 mol. of butyl borate was added for each 2 mols. of hydroxyl. The mixture was placed in the distillation flask of a vacuum distillation assembly and was held at a pressure of 50 mm and heated

in an oil bath at 80°C for 15 minutes. The temperature of the oil
bath was then gradually increased to 125°C, and at the same time
the pressure was lowered to approximately 1 mm. The reaction mix-
ture was held at this temperature and pressure for 15 minutes
after distillation had practically stopped. The vacuum distillate
contained butyl alcohol, the excess butyl borate and compounds
without hydroxyl groups. The alcohols, having been converted to
non-volatile borates, remained in the distillation flask.

The alcohols were recovered from the borates by steam dis-
tillation and were found to be a relatively complex mixture. The
borate residues, remaining after the steam distillation of the al-
cohols, were diluted with petroleum ether. A solid separated from
the borate residues from portions 2 and 3. Its properties are given
later, and correspond to those given in the literature[15] for inactive
pinocarveol hydrate.

Fenchyl alcohol, if present, should have been found in por-
tions 1 and 2. None, however, was detected by the methods used
to identify it in steam distilled wood turpentine.[13]

The alcohols from portions 1 to 5 were kept at -20°C for sev-
eral weeks. Those from portion 3 yielded a small quantity of low-
melting crystalline material, data on which are given later and
point to inactive pinocarveol (5).

Non-Alcohols The vacuum distillate (containing the non-
alcohols) was thoroughly washed with water to remove butyl alcohol.
The five portions thus obtained totaled 700 g and had the following
properties:

(5) Pinocarveol (dextro) has been reported by Schmidt[15] as one of
the autoxydation products of β-pinene.

Table V.

Refractionation of Non-Alcoolhols Listed in Table IV.

(Represents 35% of the Tailings)

Fraction No.	Distillation Temperature °C. 10 mm	Refractive Index n_D^{25}	Density d_4^{20}	Methoxyl %	Ration of each fraction to whole %	Sum of Fractions %	Ratio each fraction to Total Tailings %	Ratio each Fraction to Turpentine %
1	51-65.5	1.4777	.86 About	---	3.0	3.0	1.1	0.08
2	65.5-67.0	1.4825	.8692	0.25	2.5	5.5	0.9	0.07
3	67.0-68.0	1.4828	.8801	0.52	2.2	7.7	0.8	0.06
4	68.0-80.5	---	.9195	---	9.4	17.1	3.3	0.25
5	80.5-87.5	1.4884	.9382	---	14.9	32.0	5.2	0.40
6	87.5-90.0	1.5026	.9495	---	9.7	41.7	3.4	0.26
7	90.0-91.0	1.5086	.9608	16.0	11.5	53.2	4.1	0.32
8	91.0-91.3	1.5134	.9640	18.7	21.5	74.7	7.5	0.58
9	91.3-91.8	1.5086	.9655	15.1	6.7	81.4	2.3	0.18
10	91.8-94.0	1.4886	---	---	3.2	84.6	1.1	0.08
11	94.0-95.0	1.4801	---	---	2.8	87.4	1.0	0.08
12 a/	95.0-96.0	1.4694	.9754	2.3	5.8	93.2	2.0	0.15
13 b/ (Residue)	---	1.4636	.9820	2.4	6.8	100.0	2.4	0.18
					100.0		35.1	2.69

a/ This fraction had a saponification number of 232, equivalent to 81% bornyl acetate.

b/ This fraction had a saponification number of 260, equivalent to 91% bornyl acetate.

Table IV

Non-Alcohols

Portion	Density d_4^{20}	Refractive Index n_D^{25}	% Methoxyl	Bulk distilling between °C/10 mm
1	.8956	1.4800	2.3	68°- 90°
2	.9544	1.4936	---	85°-100°
3	.9562	1.5052	16.1	88°-100°
4	.9670	1.5064	15.6	91°-105°
5	.9732	1.4712	---	95°-105°

These portions were subjected to systematic fractional distillation, and a series of fractions was obtained having the properties indicated in Table V and Figure 3.

Terpinolene. The distillation temperature curve and the refractive index curves show breaks around 5 - 8 per cent point, indicating a high concentration of a compound in this region which was identified as terpinolene by its tetrabromide.

Bornyl Acetate. The distillation temperature and density curves, Figure 3, indicate a compound had been concentrated in the region between 87 and 100 per cent points in the distillation. The sharp break in the refractive index curve indicated that a compound with a much lower refractive index was distilling just above the distillation temperature of methyl chavicol. Inactive bornyl acetate was identified in fraction 13, Table V.

The distillation temperature curve flattens out between 45 per cent and 80 per cent points (Figure 3), indicating that a considerable quantity of pure compound has separated. The refractive index curve, however, merely reaches a maximum, indicating that the product is not entirely pure. Methoxyl determinations also indicate that methyl chavicol, the principal constituent in this region, varies in purity from 75 to 89 per cent, and then back to 75 per cent again.

Methyl chavicol. The fractions 6, 7 and 8, Table V, representing 35 per cent of Table V, were systematically refractionated. Forty per cent of this distilled from 91-91.2 at 10 mm. Methoxyl determination indicated that it was 91 per cent pure methyl chavicol. Saponification indicates that this 91-91.2° cut also contained 9 per cent of bornyl acetate which had not been completely removed by fractionation because its distillation temperature was so near that of methyl chavicol.

The refractionated methyl chavicol cut had the following constants: d_4^{20}, .9665; n_D^{25}, 1.5167. It would not solidify when held at -20°C for several weeks.

Properties of the Solid Isolated from Borate Residues. The material was recrystallized several times from benzene. The following is a comparison of the properties of the purified crystals with those listed by Schmidt[15] for pinocarveol hydrate.

Material	m.p. °C.	Mol. Wt. Camphor	Combustion C	H	[a]$_D$
Recrystallized solid	182-183(corr.)	334	70.3%	10.80%	+4°
Active pinocarveol hydrate	190-191	338	70.46%	10.74%	±31°
Inactive pinocarveol hydrate	176-177	---	---	---	0°
Calculated for [$C_{10}H_{18}O_2$]$_2$	---	340	70.53%	10.67%	---

Properties of the Alcohol Separated by Cooling to -20°C.

Material	m.p. °C.	Phenyl Urethane m.p. °C.	N	m.p. °C.
Low melting crystals	below 0°	99-100(corr.)	4.95%	178-179 (corr.)
Active pinocarveol[15]	+7	88- 90	---	190-191
Inactive pinocarveol[15]	---	95- 96	---	176-177
Calculated for $C_{17}H_{21}O_2N$	---	---	5.16%	---

About 1/2 g of the alcohol was shaken with dilute sulfuric acid. A small amount of solid, m.p. 178-179°C and not present in the starting material, was obtained. Mixed melting point with the solid isolated from the borate residue gave no depression of the melting point.

Identification of Dipentene as Tetrabromide. Four grams of Fraction 10, Table III, was dissolved in a mixture of amyl alcohol and ether, cooled to 0°C and brominated by the dropwise addition of 9 g of bromine. The crystals isolated from the reaction mixture were recrystallized from absolute ethyl alcohol. The tetrabromide melted at 124-125°C; mixed melting point with authentic diterpene tetrabromide gave no depression.

Identification of Terpinolene Tetrabromide. The tetrabromide of Fraction 2, Table V, was prepared by the same procedure used to prepare dipentene tetrabromide. The bromide melted at 118-119°C. Mixed melting point with authentic terpinolene tetrabromide showed no depression.

Identification of Inactive Bornyl Acetate. For identification purposes, 3 g of Fraction 13, Table V, was saponified with alcoholic sodium hydroxide. On dilution with water, borneol separated and was filtered off. After drying somewhat, the crude product was sublimed to eliminate tarry material, and was then recrystallized from petroleum ether. The crystals melted at 207-208°C, but gave no depression with authentic borneol, $[a]_D = -2°$.

The alkaline solution was extracted with ether to remove tarry material, then was acidified with sulfuric acid until acid to Congo, and distilled. The distillate was made alkaline to phenolphthalein with sodium hydroxide and evaporated. The p-toluidide was prepared in the usual way, and melted at 148-149°C. No depression of the melting point resulted in a mixed melting point determination with authentic acetyl p-toluidide.

Identification of Methyl Chavicol. Five grams of the methyl chavicol cut distilling between 91.0-91.2 at 10 mm was oxidized at room temperature by shaking with 300 cc of 4 per cent potassium permanganate. The manganese dioxide was filtered off and the filtrate was concentrated to 100 cc and acidifed with hydrochloric acid. The precipitated anisic acid was recrystallized from water and melted at 185-186°C. Mixed melting point with authentic anisic acid gave no depression.

After removal of the anisic acid by filtration, ether extraction of the concentrate yielded about a gram of crude homoanisic acid. After recrystallization from water the acid melted at 86-87°C.

Summary

Gum turpentine derived from longleaf pine (P. Palustris) was fractionally distilled, and the materials distilling below α-pinene and above β-pinene were separated. The samples of turpentine used in this investigation were the first (richer in "forerun") and last (richer in "tailings") portions, respectively, of commercial distillations of gum, and were found to contain .07 per cent of forerun and 7.7 per cent of tailings. Because of the very small quantity of "forerun" available and its relative complexity, separation into its constituents by fractional distillation was not found possible.

About two kilograms of tailings were subjected to repeated fractional distillation, and were found to have the following gross composition:

(a) About 2/5 of monocyclic hydrocarbons.

(b) About 1/5 terpene alcohols and phenols.

(c) About 2/5 consisting principally of ethers and esters.

The chemical and physical data of the final series of fractions obtained, when correlated and considered in the order of ascending distillation temperatures, showed the distribution of constituents in the tailings to be somewhat as follows:

(a) A small quantity of an unsaturated hydrocarbon having properties similar to p-menthene.

(b) Considerable dipentene (about 1/4), which appeared to contain a little d-limonene.

(c) A small quantity of terpinolene.

(d) A considerable proportion (about 1/3), consisting essentially of a mixture (approximately equal quantities) of methyl

chavicol and alcohols.

The alcohols appeared to be a relatively complex mixture. Fenchyl alcohol, one of the predominant alcohols in the tailings of steam distilled wood turpentine, could not be detected. A solid having the properties of pinocarveol hydrate was isolated, as also an alcohol, solid at low temperature and having properties similar to pinocarveol.

(e) A portion (about 1/6) which was essentially bornyl acetate, but also contained alcohols and a small quantity of alkyl ether.

(f) The remainder of the tailings contained hydroxy compounds which were in part phenolic, another alkyl ether, and esters other than bornyl acetate.

Description of fractionating assemblies adapted to vacuum fractionation is given.

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